

# CHEMICAL STRATEGIES FOR TEMPLATE SYNTHESSES OF COMPOSITE MICRO AND NANOSTRUCTURES

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### Abstract

The template method for preparing nanomaterials entails synthesis of the desired material within the pores of a porous membrane or solid. This report describes, for the first time, template-based syntheses of composite micro and nanostructures in which an outer tubule composed of one material encapsulates concentric inner tubules composed of other materials. Composites composed of concentric tubules of a variety of different conducting, insulating, semiconducting, photoconducting, and electroactive materials have been prepared. The chemical methodologies used to prepare these concentric tubular composites include sequential electroless and electrochemical metal deposition, sol-gel chemistry, chemical vapor deposition, and chemical and electropolymerizations.

The template method for preparing nanomaterials entails synthesis of monodisperse tubular and fibrillar nanostructures within the pores of a membrane or other nanoporous solid (1). Nanostructured materials of this type constitute one of the most important frontiers in materials science (1,2), and composite nanomaterials have been of particular recent interest (3-13). While the template method has been used to prepare segmented nanowires, where different segments down the length of the wire are composed of different materials (12,13), the chemically more challenging concept of synthesizing concentric tubular composites has never been reported. Synthetic strategies for preparing such concentric tubular composite structures are described here.

A conductor/insulator/conductor composite microstructure consisting of an outer gold tubule, surrounding an inner tubule of an electronically insulating polymer, surrounding an inner microwire of an electronically conductive polymer will serve to introduce the concept of sequential tubular-materials synthesis used throughout this work. These composite microstructures were synthesized in the rather large (3  $\mu\text{m}$ -dia.) pores of a polyester (1) template membrane (Figure 1A) so that the structures obtained after each synthetic step could be clearly imaged with the scanning electron microscope (Figure 1).

The outer gold tubes were prepared using an electroless deposition method (14,15) (Figure 1B). These Au tubules were then used to electropolymerize tubules of the insulating polymer poly(2,6-dimethylphenol) (PPO) (16) onto the inner surfaces of these Au tubes (Figure 1C). This electropolymerization method yields PPO tubules with ultrathin ( $\sim 50$  nm) walls (16). Nevertheless, these insulating tubes are defect-free (17). Cyclic voltammetry was used here to prove this point. Prior to deposition of the inner PPO tubules the Au tubule-containing membrane was immersed into an aqueous solution of the redox-active species  $\text{Fe}(\text{CN})_6^{3-}$  (17). The characteristic (17)  $\text{Fe}(\text{CN})_6^{3-/4-}$

voltammogram was observed at the Au tubes. After PPO deposition, no trace of this voltammetric signal could be seen, indicating that the outer Au tubules had been completely sealed by the inner PPO tubules.

An inner microwire of the electronically conductive polymer polypyrrole was then deposited down the center of each PPO tubule (Figure 1D). An electropolymerization method (18) was used. An Au film sputtered (19) onto one face of the template membrane served as the polymerization electrode. Electropolymerization using  $\text{IO}_4^{1-}$  dopant was continued until the polypyrrole microwire propagated through the entire 10  $\mu\text{m}$  thickness of the template (Figure 1D). Energy dispersive spectroscopy confirmed the presence of polypyrrole in the composite microstructures with two new peaks at 3.9 keV and 4.2 keV identified as the  $\text{L}\beta_1$  and  $\text{L}\alpha_1$  emissions peaks of iodine (Figure 2).

An alternative set of chemistries was used to prepare a second insulator/conductor/insulator composite in the much smaller (200 nm-dia.) pores of an alumina (1) template (Figure 3A). This composite consisted of an outer tubule of graphitic carbon, surrounding an inner tubule of the insulating polymer polyacrylonitrile (PAN), surrounding an inner gold nanowire. The chemistry used to prepare the carbon tubules (20) entails chemical polymerization of tubules of a precursor polymer (PAN), followed by thermal graphitization (Figure 3B). The PAN polymerization (20) was then repeated to yield PAN tubules within the carbon tubes (Figure 3C). An Au film was then sputtered (19) onto one face of the membrane. This film was used to electrodeposit Au nanowires down the centers of the inner PAN tubules (19).

An ensemble of the completed C/PAN/Au composite nanostructures is shown in Figure 3D. In this case, the template membrane was dissolved away (20), leaving the nanostructures protruding from a substrate surface like the bristles of a brush. The substrate may be either conductive (21) or insulating

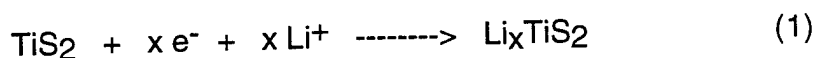
(22). Alternatively, the composite structures can be left imbedded within the pores of the template membrane (e.g., Figure 1D). Both of these approaches allow for electrical contact to be made to all of the nanostructures in parallel (14,21); this will be demonstrated below. Alternatively, the membrane can be dissolved away and the individual structures collected by filtration (18).

Chemical vapor deposition (CVD) (23) can also be used as a synthetic step to prepare such tubular composites (Figure 4). The electroless method (14,15) was used to prepare Au tubules within the 1  $\mu\text{m}$ -dia. pores of a polyester template membrane. One Au surface layer was removed (15), and the membrane was dissolved by immersion into hexafluoroisopropanol. The Au tubules (Figure 4A) were then placed in a home-built CVD reactor (24), and  $\text{TiS}_2$  tubules were deposited on the outer surfaces of the Au tubes (Figure 4B); CVD conditions - 200 mTorr  $\text{TiCl}_4$  and 600 mTorr 1-methyl-1-propanethiol, substrate temp. = 250° C, deposition time = 3 min. (24).

$\text{TiS}_2$  and other  $\text{Li}^+$ -intercalation materials are used as electrodes in Li-based batteries (25). We have recently shown that electrodes composed of template-synthesized  $\text{Li}^+$ -intercalating nanostructures provide higher discharge capacities than conventional electrodes prepared from the same material (26). These results suggest that nanomaterials may play a role in design of future Li-ion battery electrodes. However, one potential problem with this new approach for preparing such electrodes concerns the low electrical conductivities of many of the  $\text{Li}^+$ -intercalation materials (26). The CVD-based composite approach described here should solve this problem. This is because each electrode particle is coated as a thin-walled tubule onto its own current-collecting electrode (the inner Au tubule, Figure 4).

Figure 4C demonstrates this concept. An ensemble of Au/ $\text{TiS}_2$  microstructures (Figure 4B) was immersed into a 30:70 (v/v%) mixture of

ethylene carbonate and diethyl carbonate that was 1 M in LiClO<sub>4</sub>. The Au/TiS<sub>2</sub> microstructure ensemble served as the working electrode, and Li metal films were used as the reference and counter electrodes (26). Cyclic voltammetry was used to drive the following reversible Li<sup>+</sup> intercalation reaction:



The cyclic voltammogram obtained (Figure 4C) shows that Li<sup>+</sup> is reversibly inserted and removed from the outer TiS<sub>2</sub> tubules.

Finally, we have recently shown that sol-gel syntheses can be accomplished within the pores of the alumina templates to make semiconductor tubules (27). Figure 5 shows that TiO<sub>2</sub> tubules prepared in this way (27) can be filled with polypyrrole nanowires to make semiconductor/conductor composites. The polypyrrole nanowires were grown using a simple chemical polymerization method (22). TiO<sub>2</sub> is a promising material for photoelectrochemical energy production, and it has been shown that high surface area forms have higher photo efficiencies (28). TiO<sub>2</sub>/conductor nanocomposites may prove to be useful photocatalysts because the template synthesized TiO<sub>2</sub> nanostructures have very high surface areas (27). Furthermore, as discussed previously, each outer tubular TiO<sub>2</sub> catalyst particle has its own current collecting electrode inside.

A broad arsenal of chemical synthetic methodologies has been used, in sequence, to make composite tubular micro and nanostructures within the pores of various template membranes. Composites composed of a variety of different conducting, insulating, semiconducting, photoconducting, and electroactive materials have been prepared.

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### Figure Captions

Figure 1. Scanning electron micrographs of the surface of the polyester template (A) and of the tubular structures obtained after each synthetic step in the preparation of the Au/PPO/polypyrrole composite microstructures (B,C,D). (B) Surface of the template after electroless deposition of the Au tubules within the pores. (C) Surface of the template after electropolymerization of the PPO tubules within the Au tubules. Note that the PPO causes the tubule wall to be thicker than in Figure 1B. (D) After electropolymerization of the polypyrrole microwires within the PPO tubules.

Figure 2. Energy dispersive spectra before and after electropolymerization of polypyrrole into the Au/PPO composite microstructures. After polypyrrole deposition, two additional emission peaks appear in the spectra which have been assigned to iodine in  $\text{IO}_4^-$  dopant for polypyrrole.

Figure 3. Scanning electron micrographs of the surface of the alumina template (A) and of the tubular structures obtained after each step of the synthetic procedure used to prepare the C/PAN/Au composite nanostructures (B,C,D). (B) The C tubules obtained after dissolution (20) of the template. (As noted in the text, the C/PAN/Au composites were prepared by doing the appropriate chemistries in sequence leaving the alumina template intact; however it is easier to image these extremely small structures after dissolving the template.) (C) As per (B), but after polymerization of a PAN tube within each C tubule. Note that the PAN causes the tubule wall to be thicker than in Figure 3B. (D) After electrodeposition of a gold nanowire within each PAN tubule.

Figure 4. Scanning electron micrographs of an ensemble of Au tubules before (A) and after (B) CVD of the outer  $\text{TiS}_2$  tubules. The tubules are protruding from the substrate Au surface layer. That the material deposited was, indeed,  $\text{TiS}_2$

was confirmed using energy-dispersive spectroscopy and cyclic voltammetry (Figure 4C, scan rate =  $0.3 \text{ mV s}^{-1}$ ).

Figure 5. Scanning electron micrographs of  $\text{TiO}_2$  nanotubules prepared by sol-gel template synthesis before (A) and after (B) filling with polypyrrole nanowires.

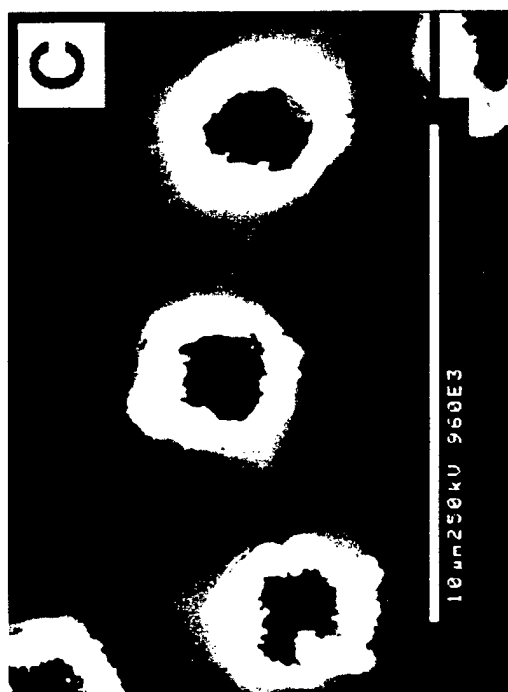
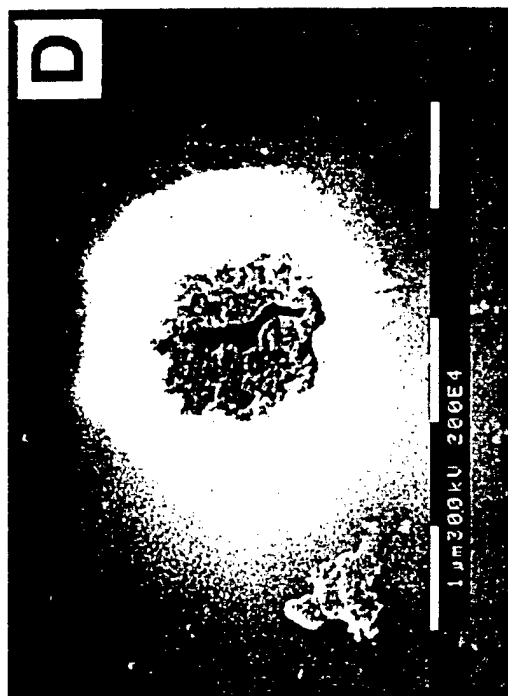
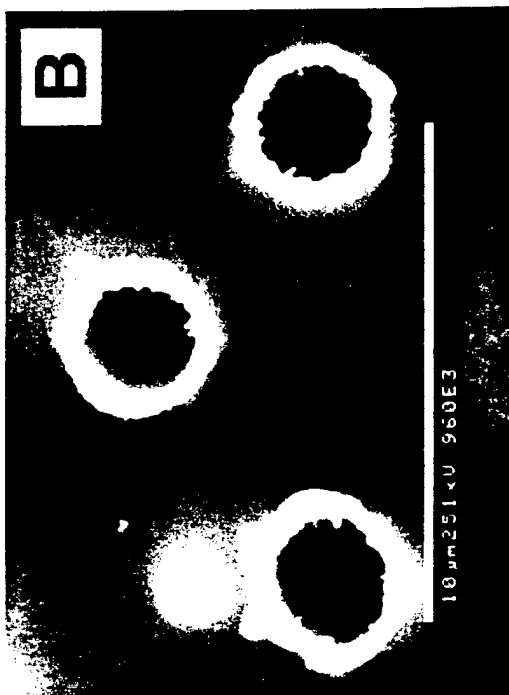


Fig 1

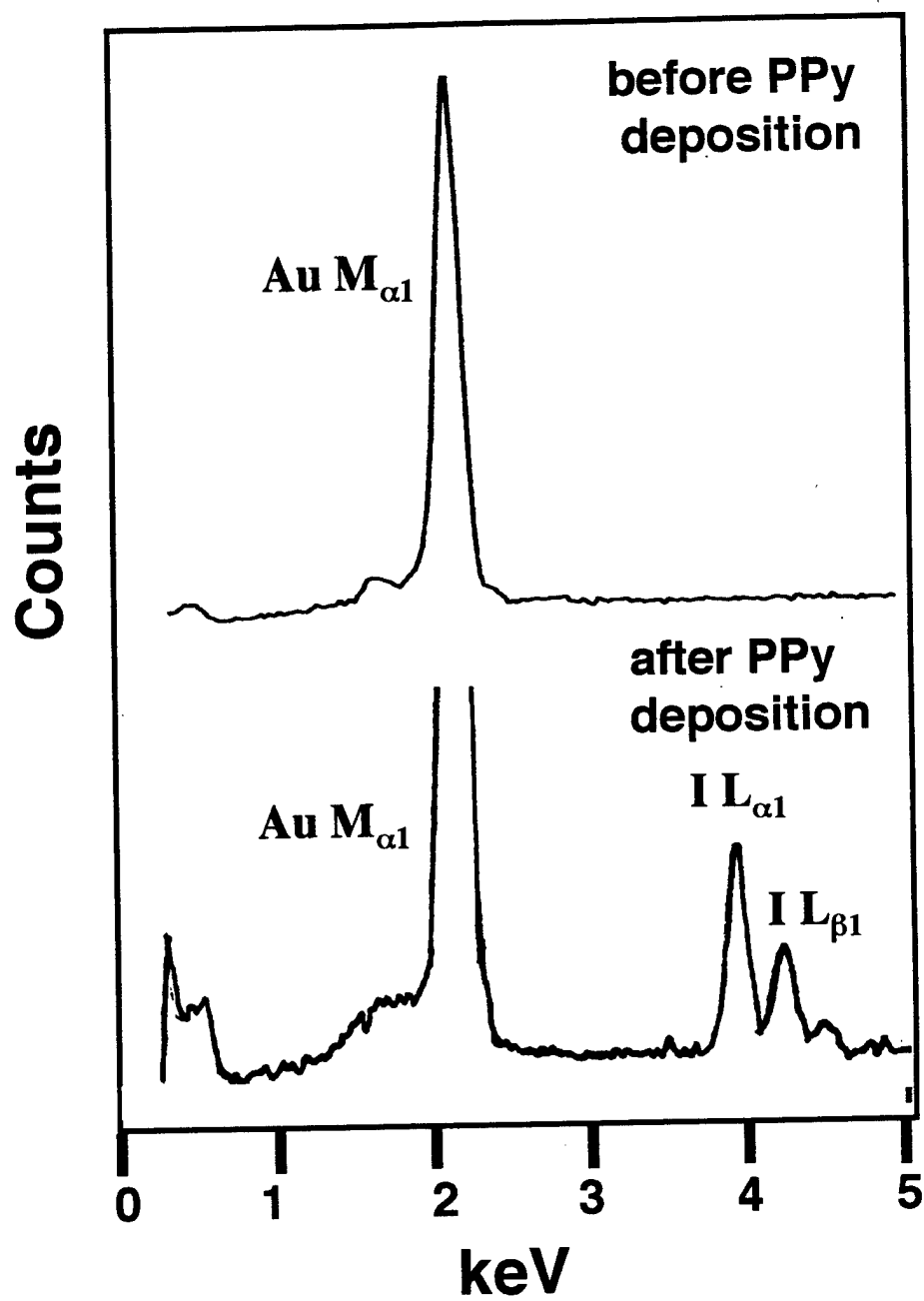


Fig 2

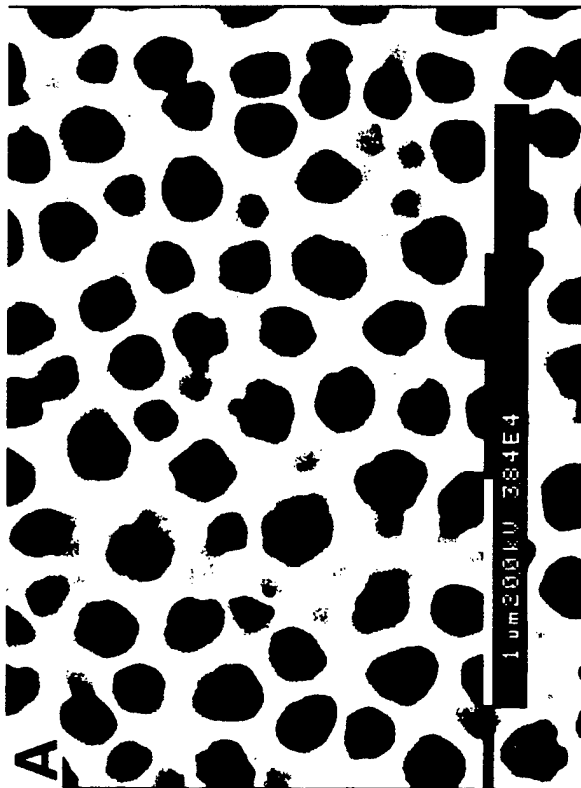
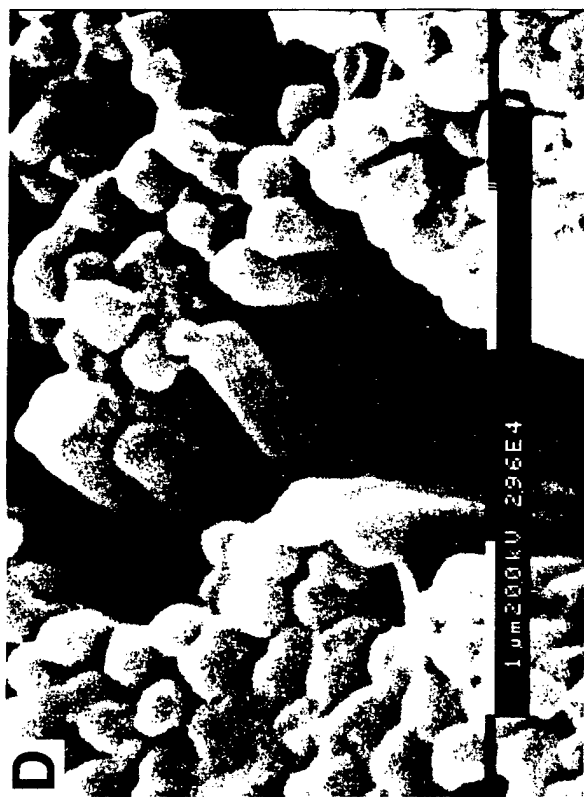
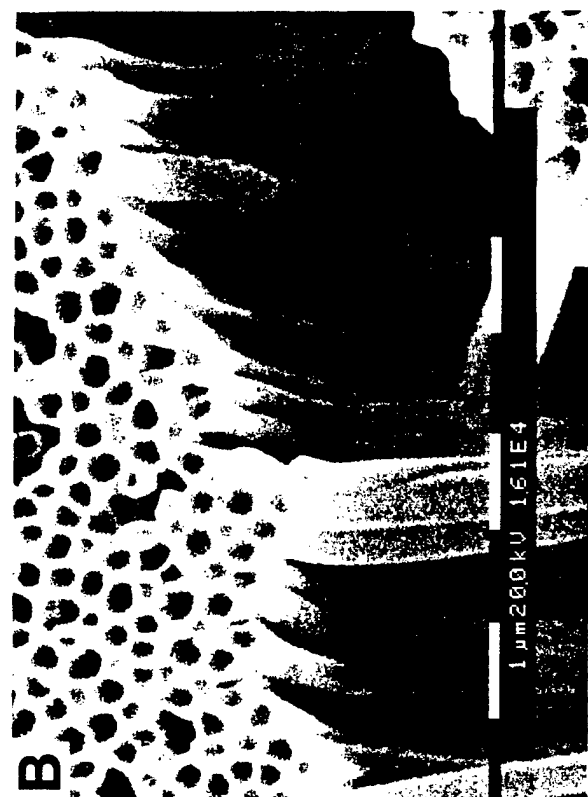


Fig. 3



FIG 4

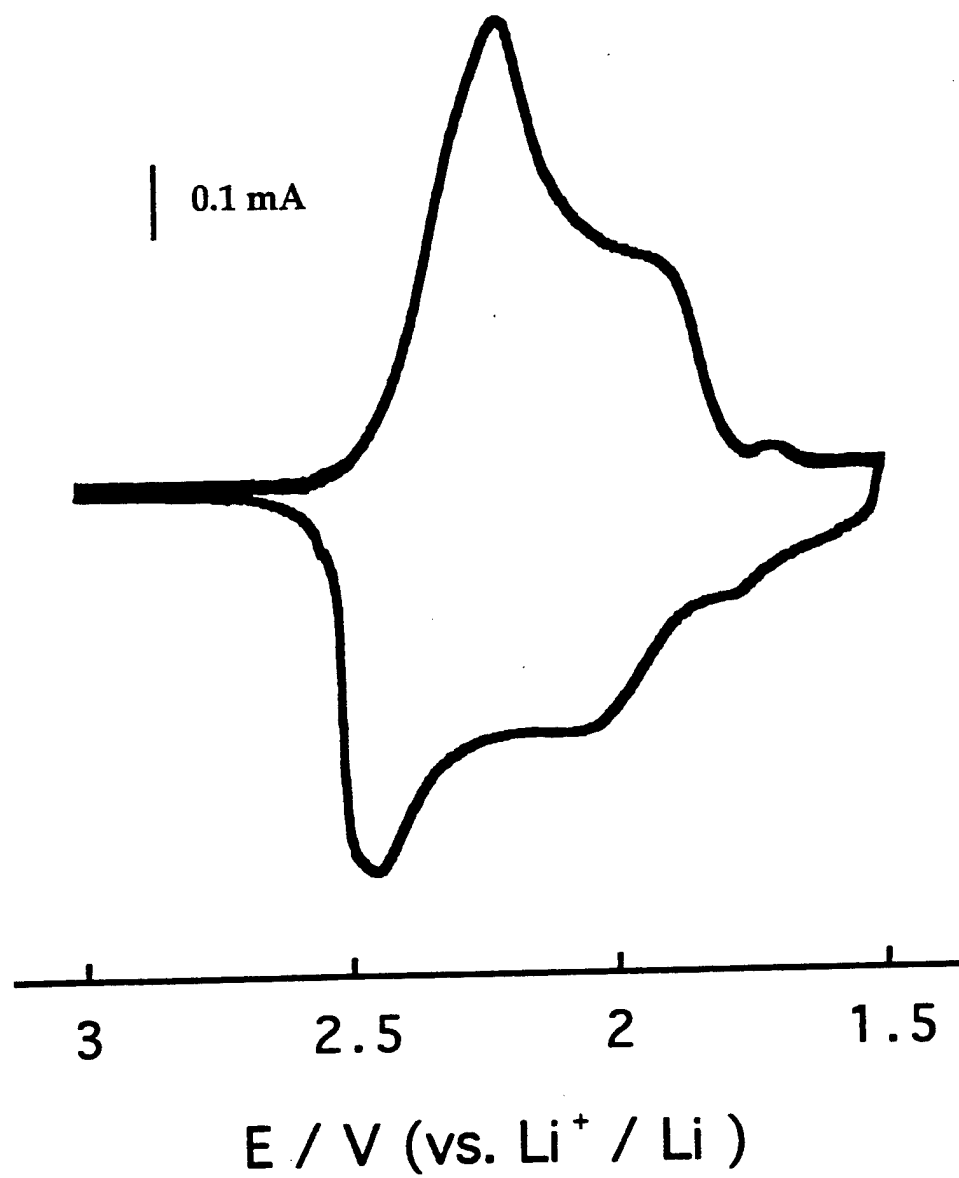
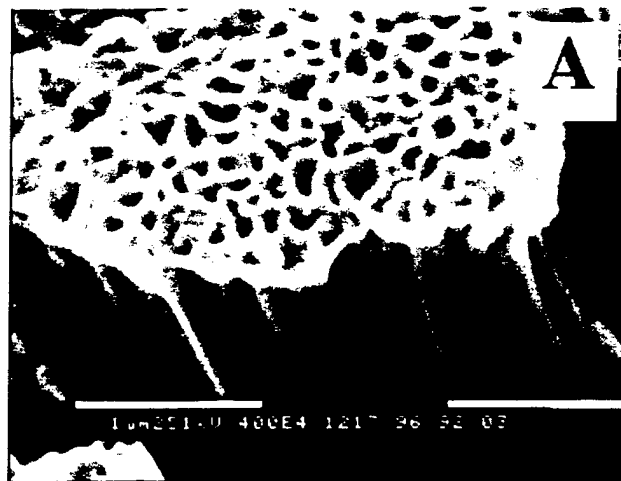


Fig 4c.





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13. Abstract: The template method for preparing nanomaterials entails synthesis of the desired material within the pores of a porous membrane or solid. This report describes, for the first time, template-based syntheses of composite micro and nanostructures in which an outer tubule composed of one material encapsulates concentric inner tubules composed of other materials. Composites composed of concentric tubules of a variety of different conducting, insulating, semiconducting, photoconducting, and electroactive materials have been prepared. The chemical methodologies used to prepare these concentric tubular composites include sequential electroless and electrochemical metal deposition, sol-gel chemistry, chemical vapor deposition, and chemical and electropolymerizations.

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